Gas-Phase Reactions of $ClONO_2$ with $Cl^-(D_2O)_{n=0-3}$ and NO_2^-

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Received: January 7, 1997; In Final Form: August 18, 1997[⊗]

The reactions of $ClONO_2$ with the $Cl^-(D_2O)_{n\leq 3}$ and NO_2^- ions were studied in a flow-tube apparatus at several temperatures in the range 170−298 K and at a helium buffer gas pressure of 0.28 Torr. Rate constants for these reactions were determined, establishing that all these ions react quite efficiently with $ClONO_2$. The product ions observed in reaction sequences are reported, and reaction mechanisms are proposed to account for the findings. In the case of Cl^- and NO_2^- the main product ion is NO_3^-, while the hydrates $Cl^-(D_2O)_{n\leq 1-3}$ lead to production of the hydrated species, $NO_3^-(D_2O)_{m\leq n-1}$. The main features of the observed secondary reactions can be described in terms of adduct formation and ligand switching. Limits on the bond energy of $(NO_3ClNO_3)^-$, 14.6 kcal/mol $\leq D(NO_3^- - ClONO_2) \leq$ 26 kcal/mol, were determined. Finally, implications of these studies to atmospheric chemistry are discussed.

Introduction

Both NO_2 and $ClONO_2$ are important components of the reactive nitrogen reservoir; they play an important role in the polar chemistry and are directly involved in the mechanism of ozone destruction in the Antarctic stratosphere.[1] Heterogeneous reactions within or on the aerosol particles are thought to convert the relatively unreactive reservoir species such as $ClONO_2$ and HCl into more active forms, Cl_2 and HOCl, which are photolyzed easily by sunlight to give Cl radicals that can catalyze ozone destruction.[2] In this respect, the reaction

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \qquad (1)$$

is particularly important and its mechanism has evoked considerable interest in various laboratories.[3] Although reaction 1 is extremely slow in the gas phase[4] ($k < 10^{-19}$ cm^3/s), it is very efficient on water−ice and water-rich surfaces.[3a−d] It has been suggested[3a,e] that ionic mechanisms could be involved in the heterogeneous chemistry of the $ClONO_2$/HCl system on stratospheric aerosol particles. HCl molecules are expected to exist at least partially dissociatively ionized, as $Cl^-(H_2O)_n$ in an ice environment.[3f,5] Thus, it is important to examine the chemistry of the $Cl^-(H_2O)_n/ClONO_2$ ion/molecule reactions in order to understand what effect these systems might have on the mechanisms of ozone destruction. In a previous experimental and theoretical study,[6] the evidence for the rapid gas-phase reaction of Cl^- with $ClONO_2$ has been presented, with a rate constant $k = (9.2 \pm 3) \times 10^{-10}$ cm^3/s at room temperature. This value is much larger than that of $k = (9.6 \pm 1) \times 10^{-12}$ cm^3/s, determined[7] recently for the Cl/$ClONO_2$ reaction of neutral species. In the present work, the reactivities of the $Cl^-(D_2O)_{n=0-3}$ and NO_2^- ions toward $ClONO_2$ at stratospheric temperatures are investigated. We have previously reported[8] the results of experimental studies on the cationic and anionic water cluster reactions with N_2O_5, DNO_3, Cl_2O, and NO. A motivating factor in these studies is, in part, an interest in the possible ionic mechanisms in heterogeneous reactions that may be of importance in stratospheric chemistry. To the best of our knowledge, there has been no prior report of the reactivity of hydrated Cl^- ions with $ClONO_2$.

Experimental Section

All experiments were performed with a temperature variable fast flow-tube (FT) apparatus, which has been described in detail elsewhere;[8b,c,9] hence, only a brief overview is presented here. The reactant ion Cl^- was formed by discharge ionization of CCl_4 in a flow-tube ion source using He as the buffer gas. The NO_2^- ions were created when air (passed through liquid N_2) was added to the carrier gas. To produce the hydrates, $Cl^-(D_2O)_n$, a small amount of D_2O was added to the CCl_4/He mixture. After formation, the ions were carried out by He from the ion source into the FT, where they react with preselected concentrations of $ClONO_2$. The precursor and product ions were mass analyzed by scanning the quadrupole mass spectrometer, and ions were detected with a channeltron electron multiplier. The rate constants were measured in the usual way from the slope of the relative decrease in reactant ion intensity with increasing $ClONO_2$ flow rate, using ion velocity values directly determined in pulsing experiments as described earlier.[9a] Typical operating conditions encompassed a total FT gas pressure of about 0.28 Torr, a buffer gas (He) flow rate of 7×10^3 sccm, and FT temperatures ranging from 170 to 298 K. The FT temperature was controlled within an accuracy of ±1 °C.

The $ClONO_2$ was synthesized by the reaction of Cl_2O with N_2O_5 on the basis of the method of Schmeisser[10] and then purified. The Cl_2O and N_2O_5 were synthesized and purified by procedures described previously.[8b,e] Care was taken to eliminate all moisture from the synthesis apparatus and the experimental gas inlet in order to minimize the heterogeneous reactions: $N_2O_5 + H_2O \rightarrow 2HNO_3$, $Cl_2O + H_2O \rightarrow 2HOCl$, and $ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$. The $ClONO_2$ samples were stored in the dark at liquid nitrogen temperature to prevent decomposition. The purity of the $ClONO_2$ samples was analyzed using the charge-transfer reaction(s) of O_2^+ with $ClONO_2$ + impurities (Cl_2, Cl_2O, HNO_3). The ionization potential[11] of O_2 (12.071 eV) is higher than those of Cl_2 (11.48 eV), Cl_2O (10.94 eV), and HNO_3 (11.95 eV). No Cl_2^+ and Cl_2O^+ signals have been found in the mass spectra (Figure 1) of our purified $ClONO_2$ samples in the FT. Therefore, we believe the impurity levels of Cl_2 and Cl_2O in $ClONO_2$ to be <0.2%. We attribute the major ion NO_2^+, together with a small amount of NO^+ detected in the spectra (Figure 1), to the dissociative charge-transfer reactions

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[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S1089-5639(97)00114-X CCC: $14.00

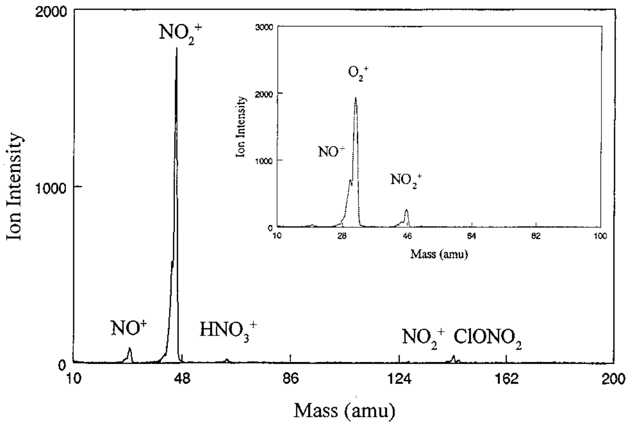


Figure 1. Mass spectra registered before (inset) and after addition through the Teflon line of 70 sccm of the $ClONO_2$/He mixture into the flow tube by eluting the $ClONO_2$ vapor with a stream of He from the cooled trap at 156 K (procedure 1; see Experimental Section). Flow tube temperature is 180 K, and flow tube pressure is 0.28 Torr.

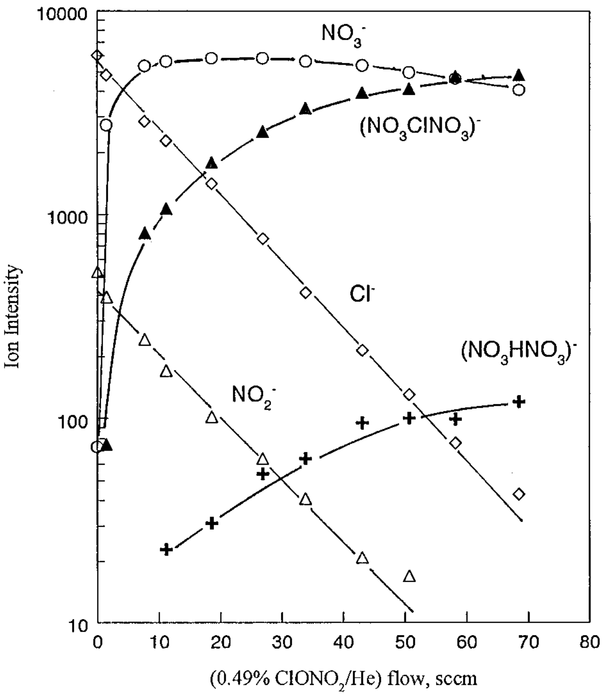


Figure 2. Observed variation of ion signals for the addition through the Teflon line of the 0.47% $ClONO_2$/He mixture into the flow tube (procedure 2). $T = 170$ K, $P = 0.28$ Torr.

$$O_2^+ + ClONO_2 \rightarrow NO_2^+ + ClO + 25.6 \text{ kcal/mol} \quad (2a)$$

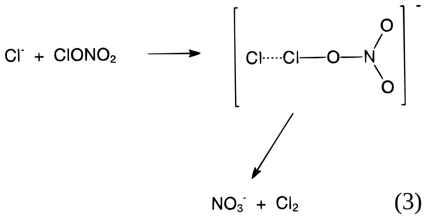
$$\rightarrow NO^+ + ClO_2 + 25 \text{ kcal/mol} \quad (2b)$$

It is worth mentioning that we also examined the $ClONO_2$ sample prepared by the reaction of Cl_2O with excess N_2O_5, and the results of the experiments were similar to those for the sample presented in Figure 1. These experiments indicate that a potential N_2O_5 impurity in our purified $ClONO_2$ samples was largely removed. The fact that no ClO^+ or ClO_2^+ signals are seen in the mass spectrum of O_2^+/($ClONO_2$ + impurities) suggests that the decomposition of $ClONO_2$ into $ClO + NO_2$ and $ClO_2 + NO$ is negligible under the present experiments. The small ion signals at *m/e* 63 and 143 are attributed to HNO_3^+ (from impurity) and $NO_2^+ClONO_2$ (from the $NO_2^+/ClONO_2$ reaction), respectively. The concentrations of XNO_3 (X = H and D) in $ClONO_2$ in the FT were determined via the termolecular reaction $NO_3^- + XNO_3 + He$ using the rate constant value from ref 8f. The relative concentrations of XNO_3 and $ClONO_2$ were also estimated by measuring the ratios of the product ions $[(NO_3XNO_3)^-]/[(NO_3ClNO_3)^-]$ from reactions 6 and 7, using the rate constant ratio $(k_6/k_7) = 0.055$ on the basis of the reported[8f,17] values and assuming the same temperature dependence. To minimize the interference of the switching reaction 14a, in both cases, the measurements were performed at low flow rates of the $ClONO_2$/He mixture. In the experiments described in this paper, at low flow rates the ratio $[(NO_3XNO_3)^-]/[(NO_3ClNO_3)^-]$ varied between 0.02 and 0.1 and the level of impurity of XNO_3 in $ClONO_2$ in the FT was <0.6%. However, when a small amount of D_2O was introduced into the ion source to produce $Cl^-(D_2O)_n$, the formation of a significant fraction of $(NO_3DNO_3)^-$ and NO_3^-DOCl, along with that of $(NO_3ClNO_3)^-$, was observed. There are various possible sources of the $(NO_3DNO_3)^-$ ion, one being that $ClONO_2$ may react with D_2O with surfaces of the FT to give DNO_3 and DOCl, the products of which may in turn become clustered to NO_3^-. We estimate that as high as 15% of $ClONO_2$ could be hydrolyzed in the FT owing to the addition of D_2O to the ion source. For this reason we used the smallest concentration of D_2O possible in the ion source for the creation of the $Cl^-(D_2O)_{n=1-3}$ ion clusters and for the measurements of their reactivities. $ClONO_2$ was introduced into the FT through a Teflon, as well as via a stainless steel, reactant gas inlet (RGI) line. Two procedures for introducing this reactant were utilized: (1) $ClONO_2$ vapor was eluted from a cooled trap at 156 K (ethanol/liquid N_2 cooling bath) with a stream of dry He (hereafter referred to as procedure 1); (2) introduction as the $ClONO_2$/He mixture (typically 0.3−0.5% $ClONO_2$/He) prepared in a 1 L glass reservoir and during the experiments stored at 273 K using an ice bath (referred to as procedure 2). In both cases the flow rate of the mixture was controlled with an MKS flow meter; the flow rate was calibrated using the $ClONO_2$ heat capacity reported by Miller et al.[12]

Chemicals. He (Airco, 99.5%), Cl_2 (Matheson, 99.99%), and O_2 (Linde, 99.9%) were used without further purification.

Results and Discussion

Reactions of $Cl^-(D_2O)_{n=0-3}$. The observed reactivity of Cl^- with $ClONO_2$ is illustrated by the data shown in Figure 2. The primary ion from the $Cl^-/ClONO_2$ reaction is NO_3^- (Figures 2−4). This observation is in agreement with the earlier study[6] showing that this product ion is formed by reaction 3.



(3)

The presence of HNO_3 could lead to the formation of a low-intensity ion complex $(NO_3HNO_3)^-$, which is observed along with the major product $(NO_3ClNO_3)^-$ (Figures 2−4). In the absence of hydrated NO_3^- complexes, the latter product ion must arise via a three-body association reaction under the conditions of these experiments. However, it should be noted that HNO_3 can also lead to the NO_3^- ion product in the Cl^-/HNO_3 primary reaction ($k = 1.6 \times 10^{-9}$ cm^3/s).[16] Ab initio calculations[6] on the $Cl^-/ClONO_2$ system show that reaction 3 is initiated by the interaction of Cl^- with the positively charged Cl atom of $ClONO_2$ followed by the formation of the intermediate ion−molecule complex, $Cl_2{\cdot}NO_3^-$, which dissociates to the $NO_3^- + Cl_2$ products.

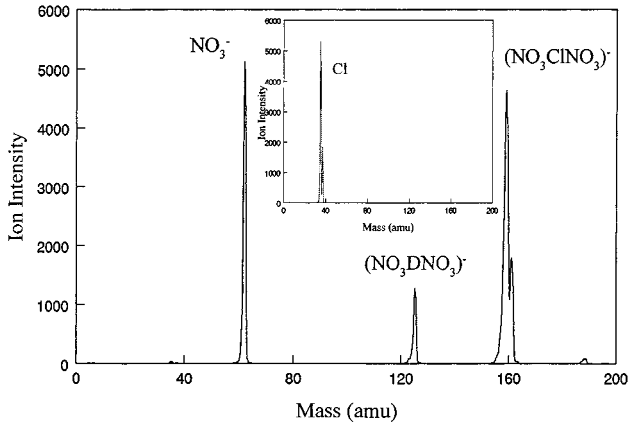


Figure 3. Mass spectra obtained before (inset) and after addition through the stainless steel line (procedure 2) of 47 sccm of the $ClONO_2$/He mixture into the flow tube at $T = 200$ K and a flow tube pressure of 0.28 Torr.

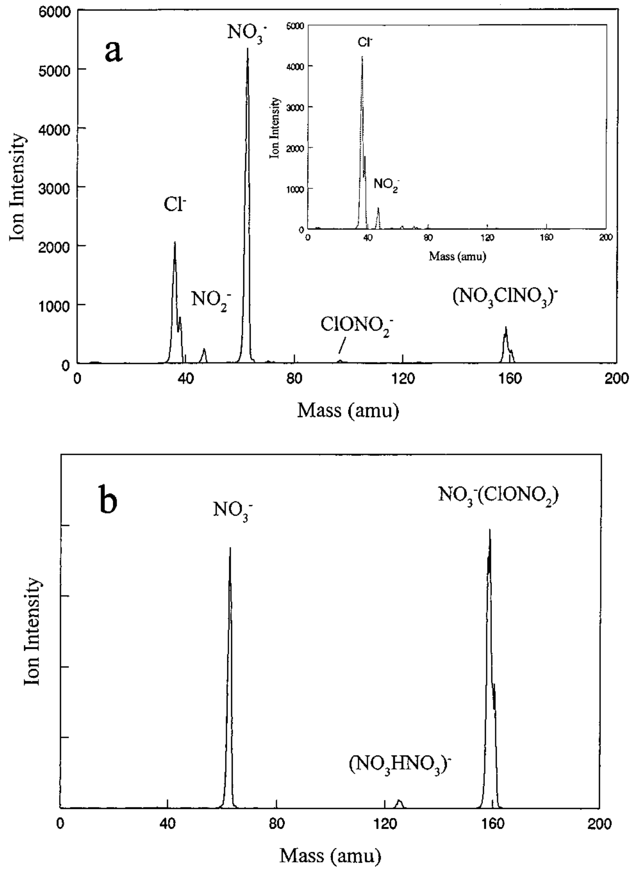


Figure 4. Mass spectra obtained before (inset) and after addition through the Teflon line (procedure 2) of 8 sccm (a) and 78 sccm (b) of the 0.49% $ClONO_2$/He mixture into the flow tube at $T = 170$ K and a flow tube pressure of 0.28 Torr.

The data in Figures 5 and 6 indicate that when the $Cl^-(D_2O)_{n=1-3}$ ions are allowed to react with $ClONO_2$, the hydrated species $NO_3^-(D_2O)_{n\leq 2}$ are formed as the primary product ions. These data suggest that the following reactions occur under the present experimental conditions

$$Cl^-(D_2O)_n + ClONO_2 \rightarrow [(D_2O)_nCl^-\cdots ClONO_2]^* \rightarrow NO_3^-(D_2O)_m + Cl_2 + (n-m)D_2O \quad (4)$$

The neutral products are not observed in the present experiments but are only inferred from the mass balance and thermochemical information.[11]

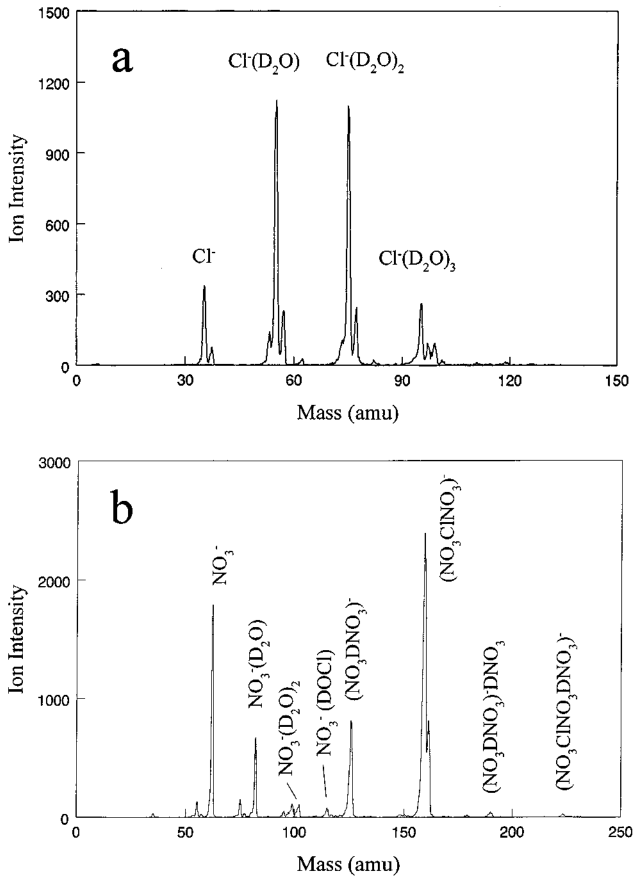


Figure 5. Mass spectra obtained before (a) and after (b) addition through the stainless steel line (procedure 2) of 20 sccm of the $ClONO_2$/He mixture into the flow tube at $T = 170$ K and a flow tube pressure of 0.28 Torr.

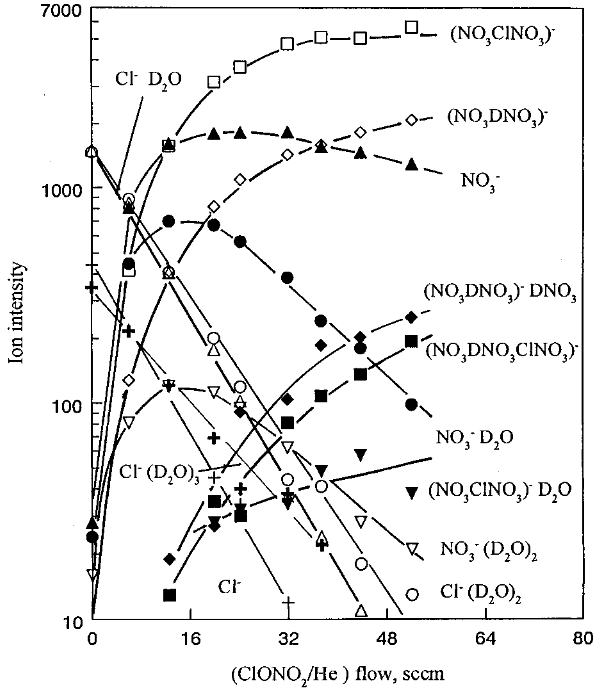


Figure 6. Observed variation of ion signals for the addition through the stainless steel line (procedure 2) of the $ClONO_2$/He mixture into the flow tube at $T = 200$ K and $P = 0.28$ Torr.

As can be seen from an examination of Table 1, reaction 4 is significantly exothermic for $(n - m) \leq 2$. However, the excited ions $NO_3^-(D_2O)_n$ when formed from these reactions have sufficient energy to dissociate in the FT by losing only one D_2O molecule. In the case of $NO_3^-(D_2O)_3$, simple RRK calculation[14] indicates that the process of dissociation by loss of two D_2O molecules is much longer than the average ion residence time in the FT.

It should be noted that any nitric acid present in the system (as impurity or from hydrolysis of $ClONO_2$) can undergo exothermic reaction 5, also leading to the $NO_3^-(D_2O)_n$ product ions:

$$Cl^-(D_2O)_n + XNO_3 \rightarrow NO_3^-(D_2O)_n + XCl \qquad (5)$$

where X = D or H.

Reactions of $NO_3^-(D_2O)_{n=0-2}$. From the data shown in Figures 2 and 4 we deduce that the primary product ion NO_3^- associatively reacts with both $ClONO_2$ and HNO_3 by adduct formation as indicated by reactions 6 and 7, respectively.

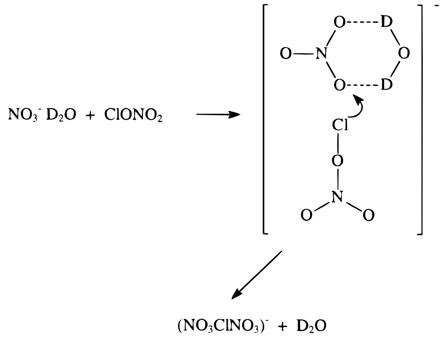
$$NO_3^- + ClONO_2 \leftrightarrow [(NO_3ClNO_3)^-]^* \xrightarrow{He} (NO_3ClNO_3)^- \qquad (6)$$

$$NO_3^- + HNO_3 \leftrightarrow [(NO_3HNO_3)^-]^* \xrightarrow{He} (NO_3HNO_3)^- \qquad (7)$$

Considering the origin of the species $(NO_3HNO_3)^-$, reaction 7 is one possibility. (Other possibilities could be reactions 9, 10a, 11b, and 14b discussed below.) On the other hand, our studies indicate that very little impurity HNO_3 is present and that the surface hydrolysis of $ClONO_2$ is expected to be slow under the present experimental conditions. Furthermore, any produced HNO_3 would be expected to remain largely adsorbed on the walls of the flow tubes. Reaction 6 has been observed previously, and the rate constant values at 232 K in H_2 ($k = 3 \times 10^{-10} cm^3/s$)[16a] and at 298 K in He ($k = 3 \times 10^{-11} cm^3/s$)[17] have been reported. It has been reported elsewhere[15] that reaction 7 is termolecular under FT conditions similar to those in the present study, and we anticipate that this is also in the case of reaction 6.

When the hydrated ion $NO_3^-(D_2O)$ is produced as a result of the $Cl^-(D_2O)_n/ClONO_2$ reactions discussed above, another possible pathway, leading to the formation of $(NO_3ClNO_3)^-$ and $(NO_3DNO_3)^-$ complexes, is D_2O displacement from $NO_3^-(D_2O)$ by $ClONO_2$ and DNO_3, respectively. Such reactions previously have been observed in other laboratories.[13,16] It should be mentioned that in the case of the $Cl^-(D_2O)_n/ClONO_2$ study, the formation of the $NO_3^-(DOCl)$ complex is also observed, but at 200 K, its intensity is much lower than that of $(NO_3DNO_3)^-$ (see Figure 5b). However, at temperatures about 170 K the intensities of $NO_3^-(DOCl)$ and $(NO_3DNO_3)^-$ are comparable.

A possible mechanism for the $NO_3^-D_2O/ClONO_2$ reaction is as follows.



(8)

Ab initio calculations[18] on $NO_3^-(H_2O)_{n=1-3}$ indicate that the oxygen atom(s) of NO_3^- forming hydrogen bond(s) with water molecule(s) draw(s) more negative charge than other oxygen(s) of NO_3^-. Hence, it might be expected that such oxygen atom(s) would be the most likely site(s) for the initial attack on the positively charged Cl atom of $ClONO_2$ to form the intermediate similar to that in reaction 8. It is likely that the analogous intermediate structure is also involved in the well-known displacement reaction 9, which is evident from the data in Figure 6.

TABLE 1: Enthalpy Changes, Δ*H* (kcal/mol),[a] for the Reaction $Cl^-\cdot(D_2O)_n + ClONO_2 \rightarrow NO_3^-\cdot(D_2O)_m + Cl_2 + (n - m)D_2O$

	m			
n	0	1	2	3
0	−25.5			
1	−10.6	−25.2		
2	2.3	−12.3	−26.6	
3	14.0	−0.6	−14.9	−28.7

[a] All Δ*H* values were estimated on the basis of the thermodynamic data cited in ref 11.

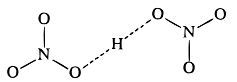
$$NO_3^-D_2O + DNO_3 \rightarrow (NO_3DNO_3)^- + D_2O \qquad (9)$$

We cannot rule out the reaction

$$NO_3^-D_2O + ClONO_2 \rightarrow (NO_3DNO_3)^- + DOCl \qquad (10a)$$

$$\rightarrow NO_3^-DOCl + DNO_3 \qquad (10b)$$

Although SIFT experiments by van Doren et al.[16b] did not show the occurrence of reaction 10, Schindler et al.[16c] did observe this reaction utilizing ICR. Recent ab initio calculations[19] by Doyle and Dunlap indicate that the C_{2h} isomer shown below, which has its C_2 axis perpendicular to the plane of molecule, is the lowest energy structure of the $(NO_3HNO_3)^-$ system.



This isomer is almost isoenergetic with an isomer having a C_2 *structure*, which has its C_2 axis in the plane of the molecule.

A related possibility (also not seen by Van Doren et al.[16b]) is the reaction of the product ion $(NO_3ClONO_2)^-$ with water vapor, which might occur, since this ion is in large abundance:

$$(NO_3ClONO_2)^- + D_2O \rightarrow NO_3^-DOCl + DNO_3 \qquad (11a)$$

$$\rightarrow (NO_3DNO_3)^- + DOCl \qquad (11b)$$

The data in Figure 6 shows that the total intensities of the NO_3^-, $(NO_3ClNO_3)^-$, and $(NO_3DNO_3)^-$ product ions exceed the intensities of the precursor ions Cl^- and $Cl^-(D_2O)$. Likewise, the data in Figure 2 show that the product ion intensities may slightly exceed those of the reactants. This is most likely due to the dissociative electron attachment process:

$$e_{th}^- + ClONO_2 \rightarrow [ClONO_2^-]^* \rightarrow \text{products} \qquad (12)$$

At moderate concentration of a neutral reactant (6×10^{10} cm^{-3}), the reaction leads[20] primarily to the NO_2^- (∼50%), NO_3^- (∼30%), and ClO^- (∼20%) product ions, together with minor ions $ClONO_2^-$ (≤2%) and Cl^- (≤6%) whose origin is not clear.

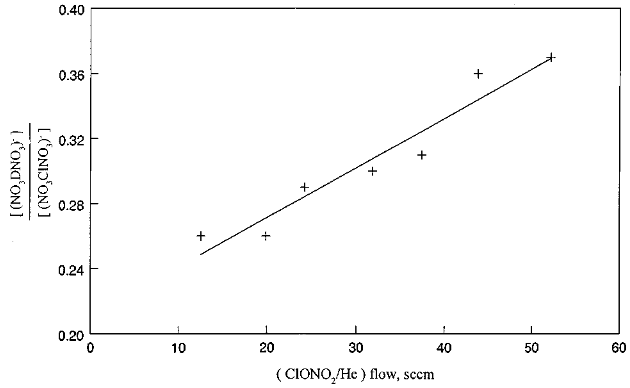
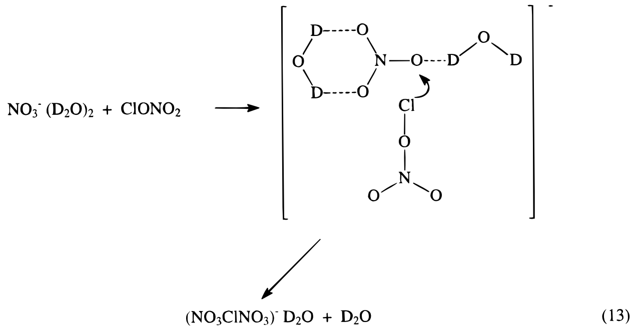


Figure 7. Observed variation of the ratio $[(NO_3DNO_3)^-]/[(NO_3\text{-}ClNO_3)^-]$ with flow rate of the $ClONO_2$/He mixture introduced into the flow tube through the stainless steel line (procedure 2) at $T = 200$K and $P = 0.28$ Torr.

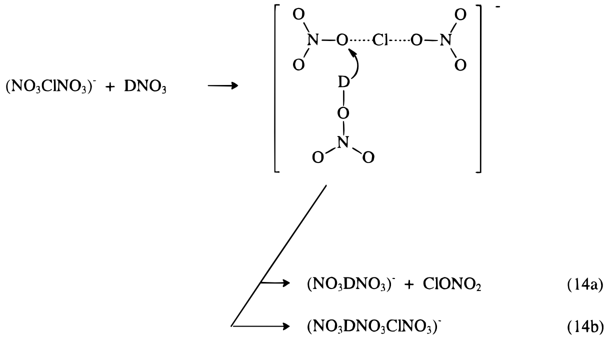
At higher $ClONO_2$ concentration (6×10^{11} cm^{-3}) the NO_2^-, ClO^-, and Cl^- ions quickly react with $ClONO_2$, leading to NO_3^- and clusters of NO_3^- with $ClONO_2$ and the impurity HNO_3.[20] The rate constant values ($k = 3.9 \times 10^{-9}$ cm^3/s,[21] $k = 1.1 \times 10^{-7}$ cm^3/s [20]) reported for electron attachment to $ClONO_2$ suggest that such a process could be important in the present case if the density of free electrons in the afterglow is relatively high. In contrast to the NO_2^-/Cl_2O study,[8e] in the present measurements our attempts to eliminate the observed effect (Figure 6 and, to a much lesser extent, Figure 2) by minimization of the discharge ionization in a flow-tube ion source were not very successful presumably because of the much higher efficiency of electron attachment to $ClONO_2$ compared with Cl_2O ($k = 2.6 \times 10^{-10}$ cm^3/s).[22] Any NO_3^- ions produced by direct dissociative electron attachment process (reaction 12) or by secondary ion chemistry, similar to those arising from reaction 3, can undergo secondary reactions with $ClONO_2$ and XNO_3 (impurity) to yield the $(NO_3ClNO_3)^-$ and $(NO_3XNO_3)^-$ product ions.

The general behavior of the $NO_3^-(D_2O)_2$ ion cluster and the observed formation of $(NO_3ClONO_2)^-D_2O)$ (Figure 6) suggest that reaction 13 occurs as follows:



Observation of this reaction suggests that the bond energy $D(NO_3^-D_2O{-}ClONO_2) > D(NO_3^-D_2O{-}D_2O) = 14.3$ kcal/mol.[11b] Note that the intensity of this ion is very small in accord with its expected reactive nature toward disproportionation in analogy to reactions 11a and 11b.

Reactions of $(NO_3ClNO_3)^-$ and $(NO_3DNO_3)^-$. As can be seen in Figure 7, the observed ionic product ratio $[(NO_3\text{-}DNO_3)^-]/[(NO_3ClNO_3)^-]$ increases with the flow rate of the ($ClONO_2$/He) mixture. This could be attributed to reaction 11b, through this behavior, together with our observation of the ion at m/e 223, which could be $(NO_3ClNO_3)^-DNO_3$ and/or $(NO_3DNO_3)^-ClONO_2$ possibly due to reaction mechanisms such as those shown in reactions 146 and 15.



$$(NO_3DNO_3)^- + ClONO_2 \leftrightarrow (NO_3DNO_3)^-ClONO_2 \quad (15)$$

Both reactions 14b and 15 require collisional stabilization. It should be mentioned that the reaction 14a has been observed[16a,b] directly with a selected ion flow drift tube apparatus at 283 K. The observation of switching reactions 8 and 14a places limits on the bond energy of $(NO_3ClNO_3)^-$: 14.6 kcal/mol $<$ $D(NO_3^-{-}ClONO_2) < 26$ kcal/mol.[23] This is consistent with an energy of 21 kcal/mol calculated[24] at the higher MP2 6-31+G(d) level of theory. Formation of the $(NO_3DNO_3)^-DNO_3$ ion complex, shown in Figure 6, is possibly attributed to the well-known[8f] association reaction 16

$$(NO_3DNO_3)^- + DNO_3 \leftrightarrow (NO_3DNO_3)^-DNO_3 \quad (16)$$

However, we cannot exclude that such a complex also can be formed in the following ligand-switching reaction

$$(NO_3DNO_3)^-ClONO_2 + DNO_3 \leftrightarrow (NO_3DNO_3)^-DNO_3 + ClONO_2 \quad (17)$$

or via the reaction

$$(NO_3DNO_3)^-ClONO_2 + D_2O \rightarrow (NO_3DNO_3)^-DNO_3 + DOCl \quad (18)$$

which does not require collisional stabilization.

Reactions of NO_2^-. Our data (Figure 2) clearly indicate that NO_2^- reacts efficiently with $ClONO_2$, and the major product ion from this, as well as from that of Cl^-/ $ClONO_2$, is NO_3^-. From careful consideration of the data, we conclude that the principle reaction channel of the $NO_2^-/ClONO_2$ system is

$$NO_2^- + ClONO_2 \rightarrow NO_3^- + ClONO \quad (19a)$$

This reaction is exothermic by 14.8 kcal/mol (reaction 11a). It is worthwhile to point out that when NO_2^- is present as the reactant ion, a small amount of the $ClONO_2^-$ product ion is also observed (Figure 4a). This could be attributed to the charge transfer from NO_2^- to $ClONO_2$ by reaction channel 19b:

$$NO_2^- + ClONO_2 \rightarrow ClONO_2^- + NO_2 \quad (19b)$$

It should be mentioned that both reaction channels 19a and 19b have been observed previously by Van Doren et al.[17] and the rate constant for these channels reported as $k = (1.5 \pm 40\%) \times 10^{-9}$ cm^3/s. As can be seen in Table 2, this value is significantly larger than ours but remains within the range of experimental uncertainty. Thermochemical information indicates that dissociation of $ClONO_2$ from channel 19b into $NO_3^- + Cl$ or $Cl^- + NO_3$ is not energetically accessible. The observation of

TABLE 2: Rate Constants[a] for the Reactions of $ClONO_2$ with $Cl^-(D_2O)_{n=0-3}$ and NO_2^-

reactant ion	k_{exp} this work	k_{exp} reported	k_{cal}[b]	k_{exp}/k_{cal}	T (K)
Cl^-	1.16 ± 0.3	(0.74 ± 0.3)[c,f] (1.13 ± 0.37)[d,f] (0.92 ± 0.3)[e,f]	1.39	0.83	298
	1.04 ± 0.3		1.48	0.70	200
	1.10 ± 0.2		1.53	0.72	170
$Cl^-(D_2O)$	1.04 ± 0.3		1.27	0.82	200
	0.80 ± 0.2		1.31	0.61	170
$Cl^-(D_2O)_2$	0.85 ± 0.3		1.16	0.73	200
	0.73 ± 0.2		1.19	0.61	170
$Cl^-(D_2O)_3$	0.70 ± 0.3		1.09	0.64	200
	0.61 ± 0.2		1.12	0.54	170
NO_2^-	1.01 ± 0.3	(1.5 ± 0.6)$^{+2}$	1.34	0.75	200
	0.98 ± 0.2		1.39	0.70	170

[a] Units for all rate constants are 10^{-9} cm^3/s. [b] Rate constants were calculated from the Su−Chesnavich theory,[25] using $a = 6.28$ Å^3 and $\mu_D = 0.77$ D. [c] Rate constant measured using the stainless steel gas inlet system. [d] Rate constant measured using the glass inlet system. [e] Average value from the data obtained with stainless steel and glass inlet systems. [f] Rate constant measured at 298 K.

charge transfer in reaction 19b places a limit on the electron affinity (EA) of $ClONO_2$; EA($ClONO_2$) is greater than that of NO_2^-. This is in agreement with the findings of van Doren et al.[17]

Rate Constants. The rate constants for the studied systems are summarized in Table 2. The table also includes the values reported by Okumura et al.[6] for $Cl^-/ClONO_2$ at room temperature as well as the calculated ones from the Su−Chesnavich theory[25] using the calculated polarized ability[24] of 6.28×10^{-24} cm^3 and dipole moment[26] of 0.77 D. In the present experiments the k_{exp} values were obtained using the Teflon inlet line (at $T = 170$ and 298 K), the stainless steel line (at $T = 200$ K), and procedure 2. In every case these values are an average of at least four measurements, and the error limits show the statistical fluctuations. For the $Cl^-/ClONO_2$ and $NO_2^-/ClONO_2$ systems, an absolute uncertainty in the k_{exp} values can be as large as 30%, while that for $Cl^-(D_2O)_{n\,=\,1-3}/ClONO_2$ may be as high as 60%. The major factors that influence the accuracy of the measured rate constants are (1) contributions of impurities from the synthesis and/or formed in the FT and (2) interferences of products from the reactions of free electrons with $ClONO_2$ in the FT that may influence the measured slope of the ion decay plots vs $ClONO_2$ flow rate.

In the rate constant measurements of $Cl^-/ClONO_2$ and $NO_2^-/ClONO_2$, the amount of HNO_3 impurity in $ClONO_2$ introduced into the FT was estimated to be <0.6%. The presence of such a level of HNO_3 would lead to an enhancement of less than 0.4% in k_{exp} due to the Cl^-/HNO_3 reactions ($k = 1.6 \times 10^{-9}$ cm^3/s [13]) and NO_2^-/HNO_3 ($k = 1.6 \times 10^{-9}$cm^3/s [13]). However, as discussed in detail, for the $Cl^-(D_2O)_{n=1-3}/ClONO_2$ cases, when a small amount of D_2O was introduced into the ion source to produce the hydrated reactant ions $Cl^-(D_2O)_{n=1-3}$, the concentration of nitric acid (DNO_3) might significantly increase owing to the hydrolysis of $ClONO_2$ in the FT. This could lead to observation of higher k_{exp} values (up to 10%). Since we did not find any evidence for the $Cl^-(D_2O)_{n=0-3}/DOCl$ reactions in the present experiments, it was assumed that the DOCl formed from the hydrolysis of $ClONO_2$ does not affect our measured rate constants for $Cl^-(D_2O)_{n=1-3}/ClONO_2$. In the case of $Cl^-/ClONO_2$ and $NO_2^-/ClONO_2$, the interference of Cl^- and NO_2^-, respectively, from reactions with free electrons cannot be excluded. In the present study, we varied ion-source conditions in order to obtain evidence for such a possibility. In some measurements, at low flow rates (<20 sccm) the decrease of Cl^- with the $ClONO_2$ concentration was observed to be lower than that at higher flow rates where the decrease is linear. Such behavior may suggest that Cl^- could be produced in the FT by interaction with free electrons. For the experiments described here, this effect was minimized (Figures 2 and 6) by optimizing the discharge in the ion source. Therefore, we believe that channel 12 is not a significant contributor to the errors in the measured values of k_{exp} for $Cl^-/ClONO_2$. As seen in Table 2, k_{exp} for this reaction is very close to the value of Okumura et al.[6] determined when $ClONO_2$ was introduced into the ICR apparatus through the glass inlet system. From the table it is evident that k_{exp} values are close to k_{cal} and that the k_{exp}/k_{cal} ratio decreases slightly with hydration. These data seem to suggest that energy barriers exist in the potential surfaces for the $Cl^-(D_2O)_{n=0-3}/ClONO_2$ reactions. Presumably, the k_{exp}/k_{cal} trend is a reflection of the solvent reorganization about the new charge distribution in the intermediate complex $[(D_2O)_nCl^-ClONO_2]$ to the observed products $NO_3^-(D_2O)_m$ + neutrals. Similarly, the $(k_{exp}/k_{cal}) = 0.75$ ratio for $NO_2^-/ClONO_2$ implies that some barrier exists for the forward reaction channel. This situation is similar to that found for the NO_2^-/N_2O_5 system, where the reaction efficiency is $k_{exp}/k_{cal} = 0.68$ at 231 K. These observations may reflect significant intramolecular rearrangements within the intermediate complexes of both reactions.

Atmospheric Implications. As already mentioned, the reaction of $ClONO_2$ with HCl is an important heterogeneous reaction on polar stratospheric clouds (PSCs), which is thought to convert the Cl trapped in both these species into an easily photolizable form, Cl_2. HCl has been proposed to exist on PSCs, at least partially, as $Cl^-(H_2O)_n$.[3f] The results presented here indicate that $Cl^-(D_2O)_{n\leq3}$ reacts quite efficiently with $ClONO_2$, leading to Cl_2 and the stable ions $NO_3^-(DNO_3)_n$ by a series of sequential reactions. The $NO_3^-(HNO_3)_{n=1,2}$ represent the dominant anions found[27] through much of the stratosphere and troposphere. Thus, it would appear that an ionic mechanism can be involved in the heterogeneous process, leading to conversion of $ClONO_2/HCl$ into Cl_2 onto PSCs. However, implying the possible importance of this mechanism in stratospheric chemistry requires caution, as well as further considerations. First, the $Cl^-(H_2O)_n/ClONO_2$ reaction efficiency decreases with increasing cluster size. The distributions of both the $Cl^-(H_2O)_n$ ion clusters and $ClONO_2$ within—or on the surface of—water droplets are difficult to predict. Second, we do not contend that the observed gas-phase reactivities of hydrated Cl^- are a direct measure of their reactivity in the condensed state of PSCs. Third, the reactivities of $Cl^-(H_2O)_n$ toward other important neutrals (e.g., HOCl and HNO_3) that are expected to be present on PSCs have not been assessed.

Conclusions

The reactivity of the $Cl^-(D_2O)_{n\leq3}$ and NO_2^- ions with $ClONO_2$ has been investigated. The efficiency of the $Cl^-(D_2O)_{n\leq3}/ClONO_2$ reactions was observed to decrease with increasing cluster size. Sequential chemistry initiated by these reactions has been presented. These reactions provide pathways for the conversion of Cl from $Cl^-(H_2O)_n/ClONO_2$ to photochemically labile Cl_2 and mechanisms for the formation of the $NO_3^-(HNO_3)_n$ ionic complexes. The $NO_2^-/ClONO_2$ reaction was found to lead predominantly to the NO_3^- ion product, but a small fraction of charge transfer in this reaction was also observed.

Acknowledgment. Financial support by the Atmospheric Sciences Division of the National Science Foundation, Grant No. ATM-9321660, is grateful acknowledged. We are also grateful to the National Science Foundation for a grant through the International Program Office, Grant No. INT-9208271.

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